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Analysis of Pyrolysis Products of a Commercial Phenolic Resin by Gas Chromatography/Mass Spectrometry

by Rose Pesce-Rodriguez and James Wolbert

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14. ABSTRACT
A commercial phenolic resin was analyzed by pyrolysis-gas chromatography/mass spectrometry. Estimates of pyrolysis products (aromatic-phenolic, aromatic-nonphenolic, and permanent gas products) as a function of pyrolysis temperature are provided.

15. SUBJECT TERMS
phenolic resin, aromatic, methane, pyrolysis, gas chromatography/mass spectrometry, GC/MS, Cellobond J2027L

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1. Introduction/Background

A sample of a commercial phenolic resin (i.e., Cellobond J2027L) was provided along with a request for an analysis of the pyrolysis products as a function of temperature. Specifically, there was an interest in the levels of permanent gas products (carbon monoxide [CO], carbon dioxide [CO_2], methane [CH_4], and water [H_2O]) as well as larger products (aromatic-phenolic and aromatic-nonphenolic) generated by pyrolysis of the resin from 200 to 1100 °C.

2. Experimental

Desorption and pyrolysis products were analyzed by means of a gas chromatography/mass spectrometry (GC/MS) instrument with a desorption interface. Desorption was achieved via a CDS Analytical Model 2000 Pyroprobe (coil type) connected through a heated interface chamber to the splitless injector of an Agilent (Santa Clara, California) GC/MS system (Model 6890N GC and Model 5973N MSD). The GC column used was a HP-5 capillary column (0.25 mm × 30 m, 0.25-µm film). The injector temperature was 200 °C; the Pyroprobe interface was set to a temperature of 250 °C. The GC oven temperature program was as follows: 100 °C isothermal for 1 min, 100–250 °C at 40 °C/min, and 250 °C isothermal for 1 min. The Pyroprobe was programmed to give a 20-s desorption pulses at a heating rate of 1,000 °C/s. The pulse temperature is based on calibration provided by the vendor and was not measured for this study. Samples (1–2 mg), which were prepared by curing Cellobond J2027L (Hexion Select) at 121 °C for 3 h in air, were held within the coil of the Pyroprobe by first placing them in a quartz tube containing a small plug of glass wool and then inserting the entire tube into the coil. Selected ion chromatograms were obtained via Hewlett Packard ChemStation software by extracting specified masses from the total ion chromatogram.

3. Results and Conclusions

Total ion chromatograms for pyrolysis of the phenolic resin are given in Figs. 1–9. Mass spectra, including best chemical identifications based on library matches, associated with each chromatogram are given in the Appendix indicated in the figure caption.

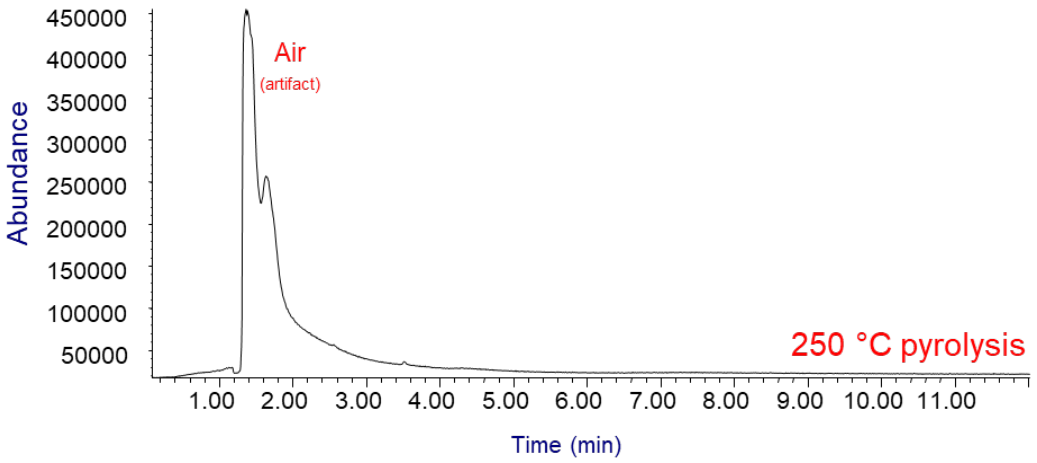

Fig. 1 Total ion chromatogram for phenolic resin when pyrolyzed at 250 °C. Mass spectra given in Appendix A.

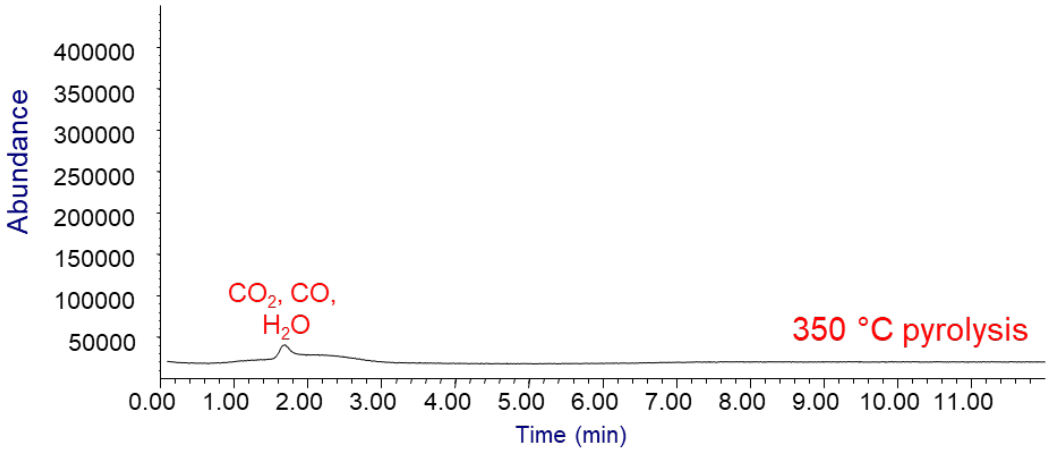

Fig. 2 Total ion chromatogram for phenolic resin when pyrolyzed at 550 °C

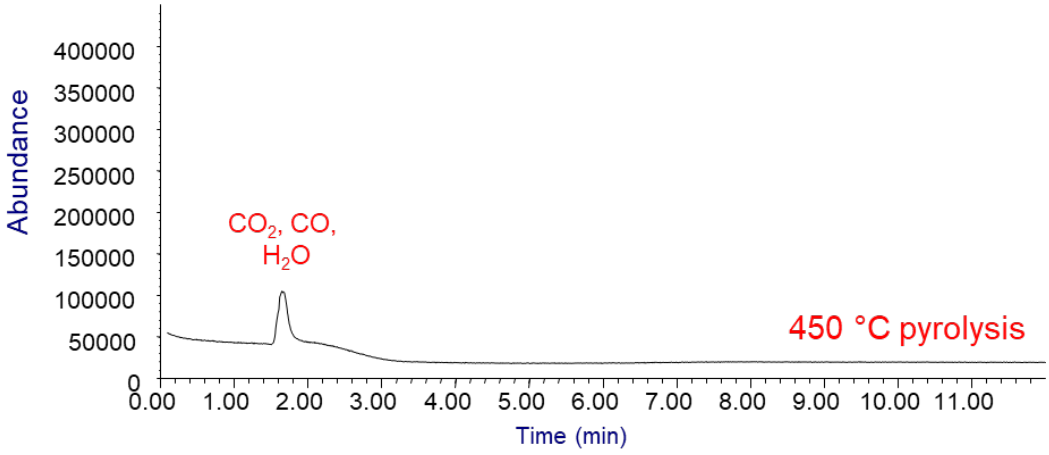

Fig. 3 Total ion chromatogram for phenolic resin when pyrolyzed at 450 °C

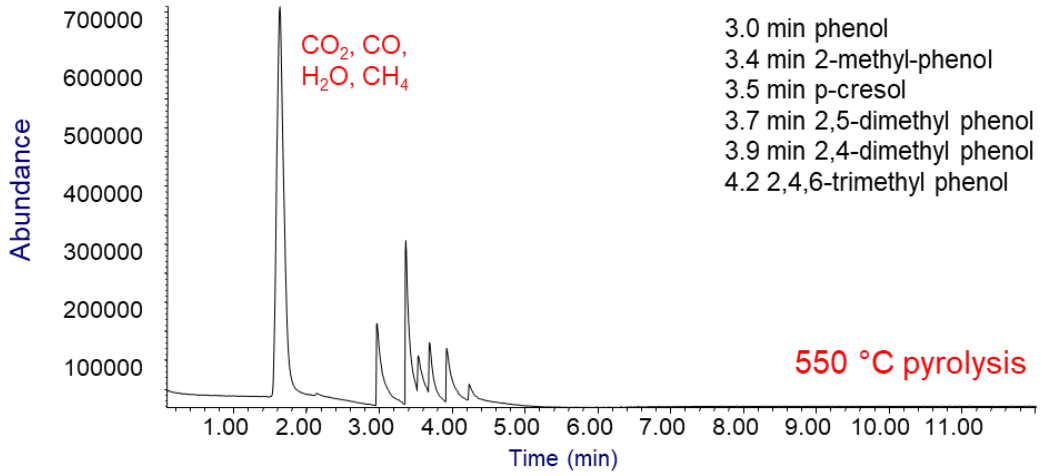

Fig. 4 Total ion chromatogram for phenolic resin when pyrolyzed at 550 °C. Assignments for peak times given in the insert. Mass spectra given in Appendix B.

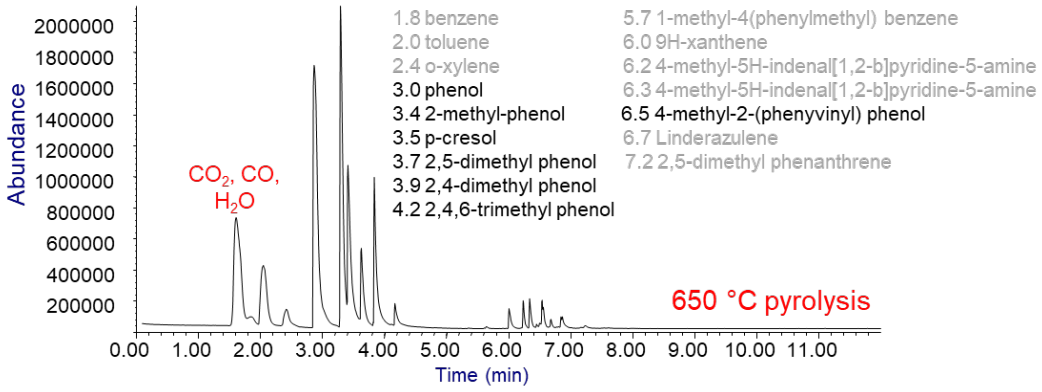

Fig. 5 Total ion chromatogram for phenolic resin when pyrolyzed at 650 °C. Assignments for peak times given in the insert. Phenolic shown in black font, non-phenolic aromatics shown in gray font. Mass spectra given in Appendix C.

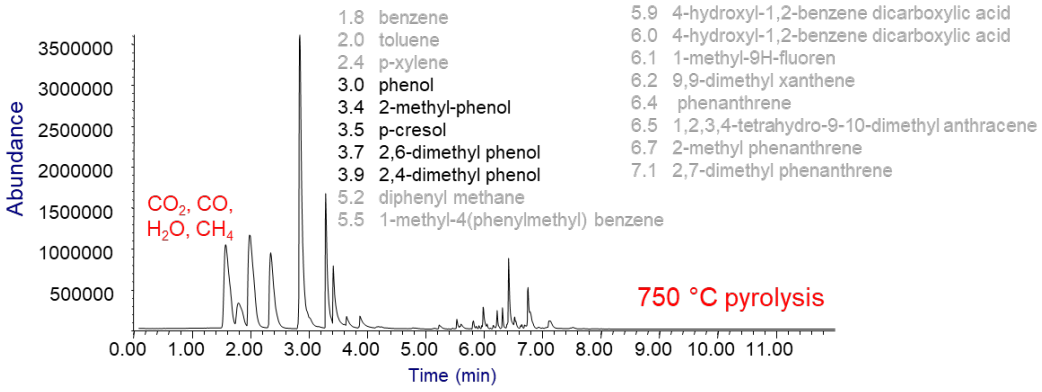

Fig. 6 Total ion chromatogram for phenolic resin when pyrolyzed at 750 °C. Assignments for peak times given in the insert. Phenolic shown in black font, non-phenolic aromatics shown in gray font. Mass spectra given in Appendix.

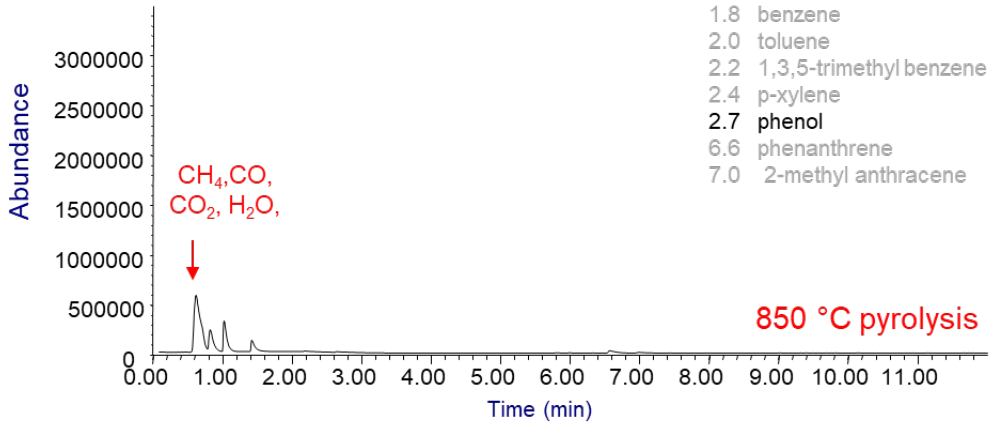

Fig. 7 Total ion chromatogram for phenolic resin when pyrolyzed at 850 °C. Assignments for peak times given in the insert. Phenolic shown in black font, non-phenolic aromatics shown in gray font. Mass spectra given in Appendix E.

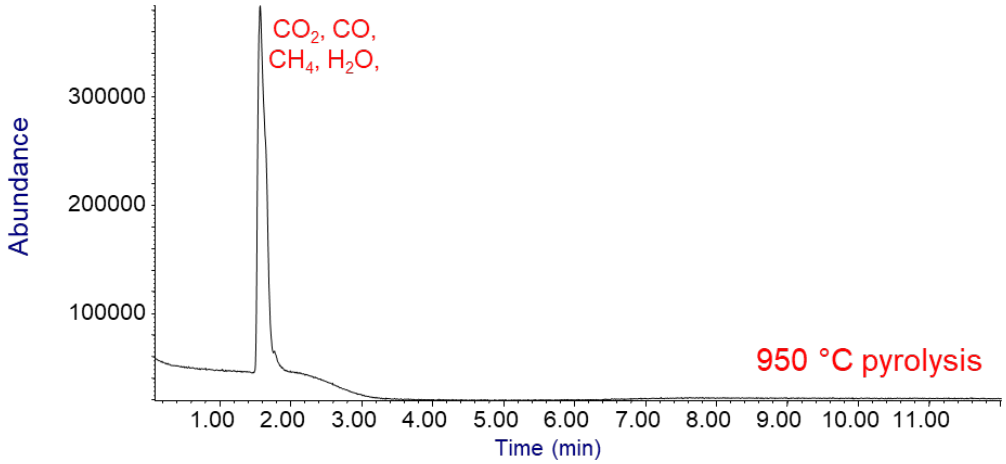

Fig. 8 Total ion chromatogram for phenolic resin when pyrolyzed at 950 °C. Mass spectra given in Appendix F.

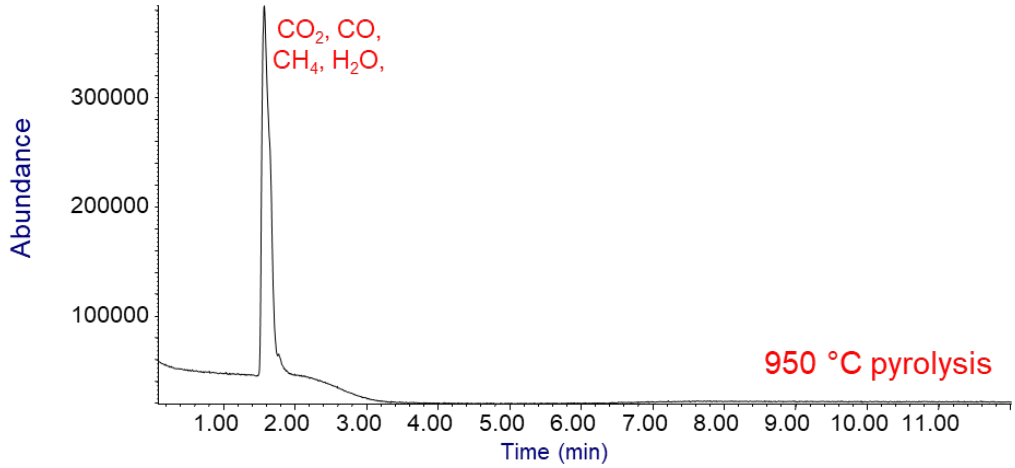

Fig. 9 Total ion chromatogram for phenolic resin when pyrolyzed at 1050 °C. Mass spectra given in Appendix G.

Figure 10 gives a rough estimate of the levels of pyrolysis products generated at each temperature. The results are in general agreement with those in Katzman et al. (1995) and Bouajila et al. (2003), except for a somewhat higher temperature at which phenolic products are generated (i.e., approximately 700 °C in the current work versus approximately 500 °C the Katzman and Bouajila studies). However, the higher temperature is consistent with phenolic pyrolysis results from other works, including Chang and Tackett (1990), Szymański et al. (2002), and Wong et al. (2015), suggesting that comparisons cannot be made without carefully comparing the resin type and its structure, which is not possible with proprietary commercial products. For the given system in this study (i.e., Cellobond J2027L), it is concluded that pyrolysis occurs as indicated in the experimental results presented in this report. It is difficult to interpret the results further without knowing the specific composition of the commercial resin. Such an analysis is beyond the scope of this very limited investigation. Nevertheless, the pyrolysis GC/MS results herein provide valuable information on the chemical stability of Cellobond J2027L and on the types of gaseous decomposition that contribute to void formations at specific temperatures from 200 to 1100 °C.

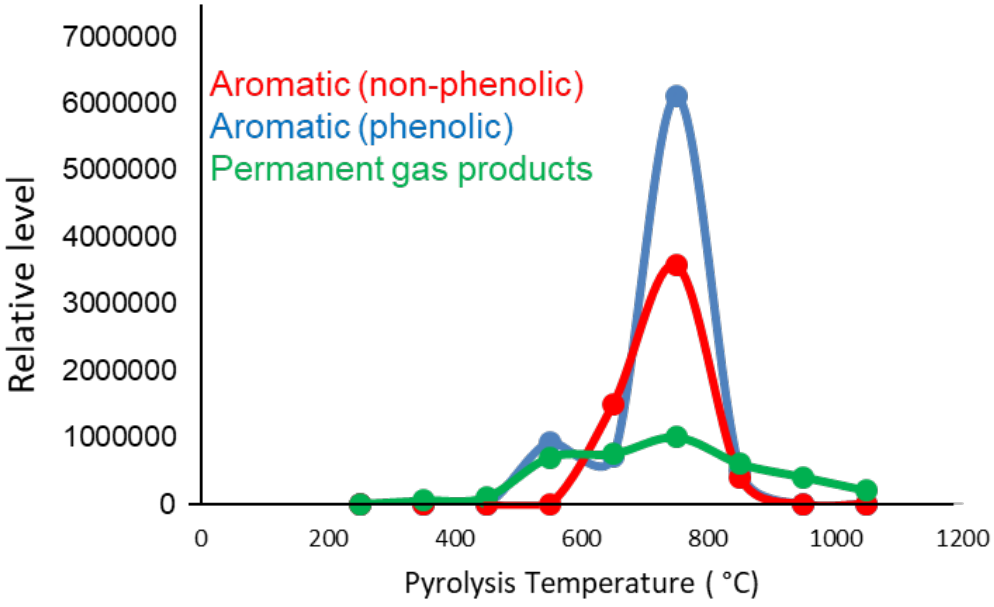

Fig. 10 Relative level of pyrolysis products platted against pyrolysis temperature. Permanent gas products are CO_2, CO, CH_4, and H_2O.

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Appendix A. Mass Spectra for 250 °C Pyrolysis

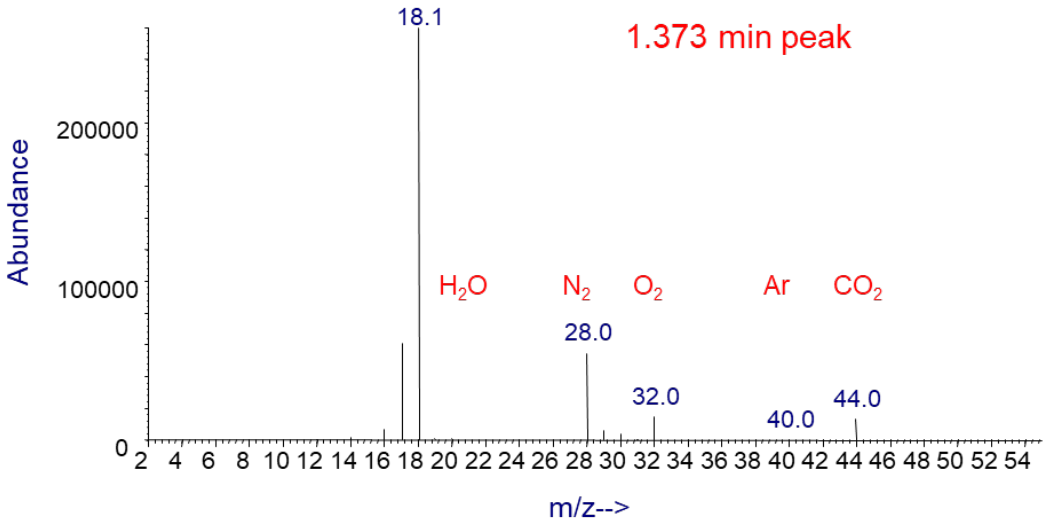


Fig. A-1 Mass spectrum of permanent gas peak from 250 °C pyrolysis of phenolic resin

Appendix B. Mass Spectra for 550 °C Pyrolysis

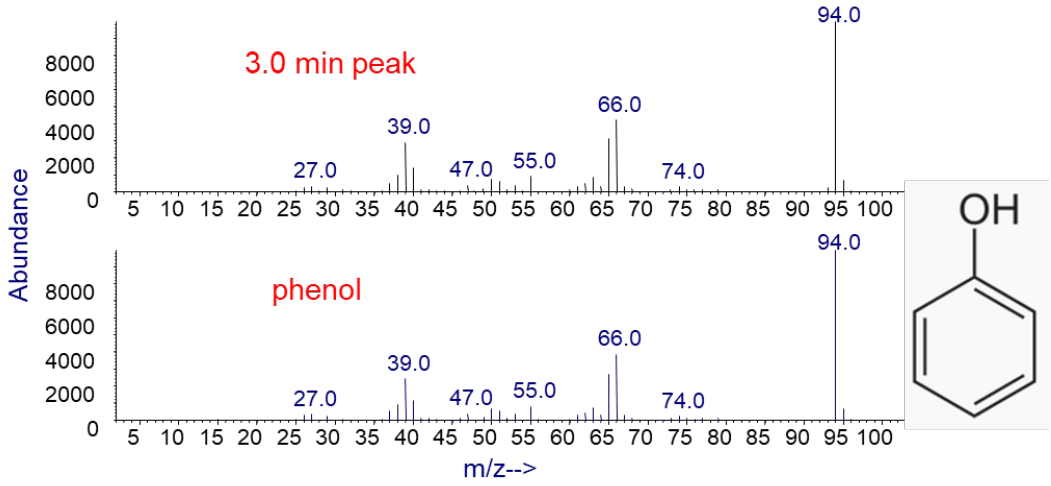


Fig. B-1 Mass spectrum and library search match (with structure) of 3.0-min peak from 550 °C pyrolysis of phenolic resin

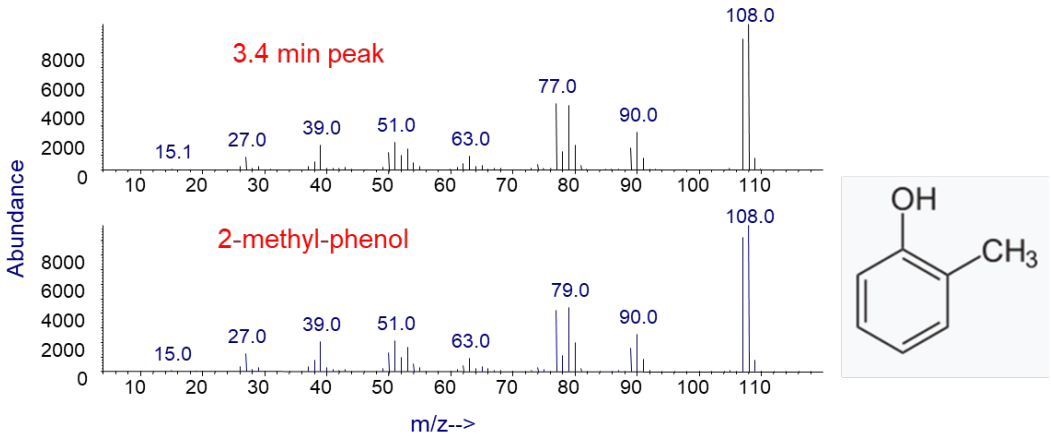


Fig. B-2 Mass spectrum and library search match (with structure) of 3.4-min peak from 550 °C pyrolysis of phenolic resin

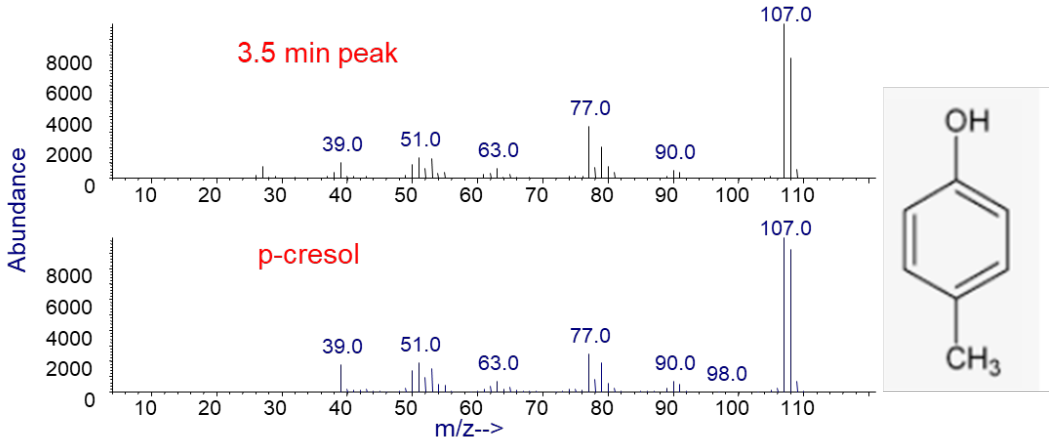


Fig. B-3 Mass spectrum and library search match (with structure) of 3.5-min peak from 550 °C pyrolysis of phenolic resin

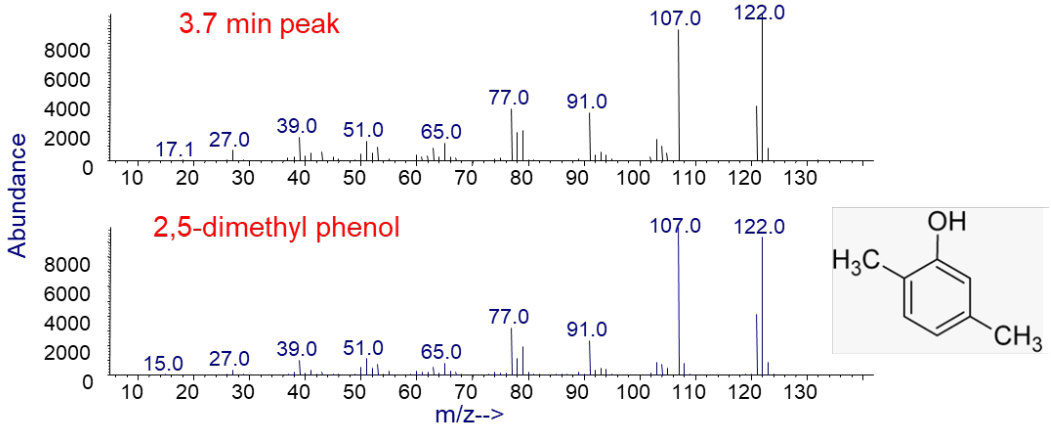


Fig. B-4 Mass spectrum and library search match (with structure) of 3.7-min peak from 550 °C pyrolysis of phenolic resin

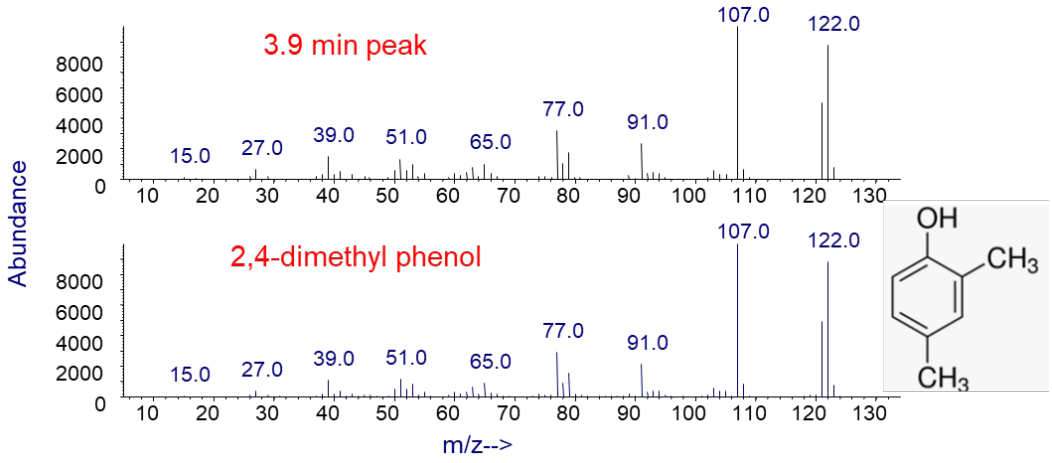


Fig. B-5 Mass spectrum and library search match (with structure) of 3.9-min peak from 550 °C pyrolysis of phenolic resin

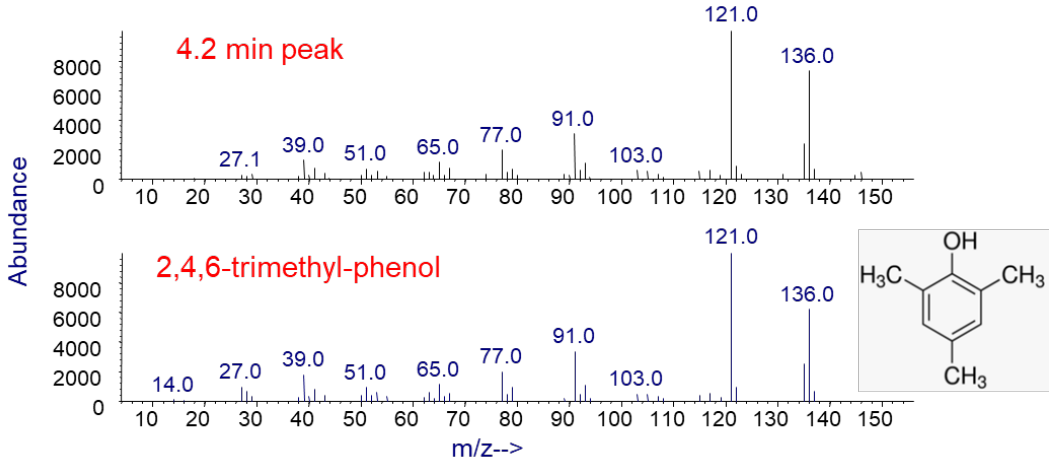


Fig. B-6 Mass spectrum and library search match (with structure) of 4.2-min peak from 550 °C pyrolysis of phenolic resin

Appendix C. Mass Spectra for 650 °C Pyrolysis

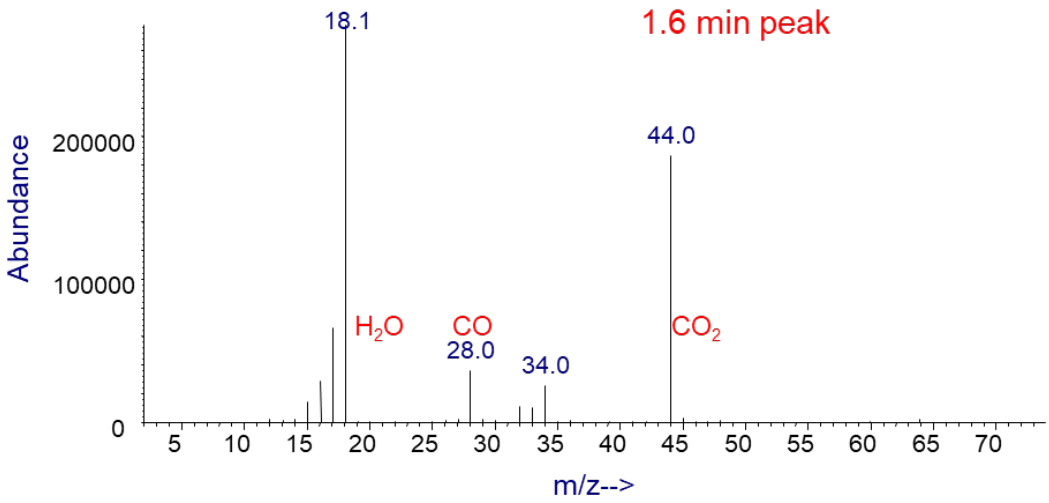


Fig. C-1 Mass spectrum of permanent gas peak from 650 °C pyrolysis of phenolic resin

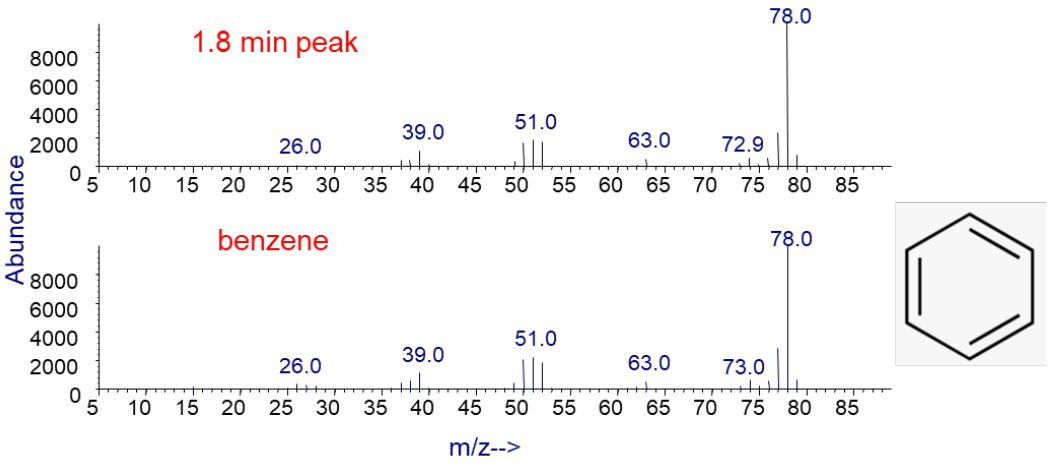


Fig. C-2 Mass spectrum and library search match (with structure) of 1.8-min peak from 650 °C pyrolysis of phenolic resin

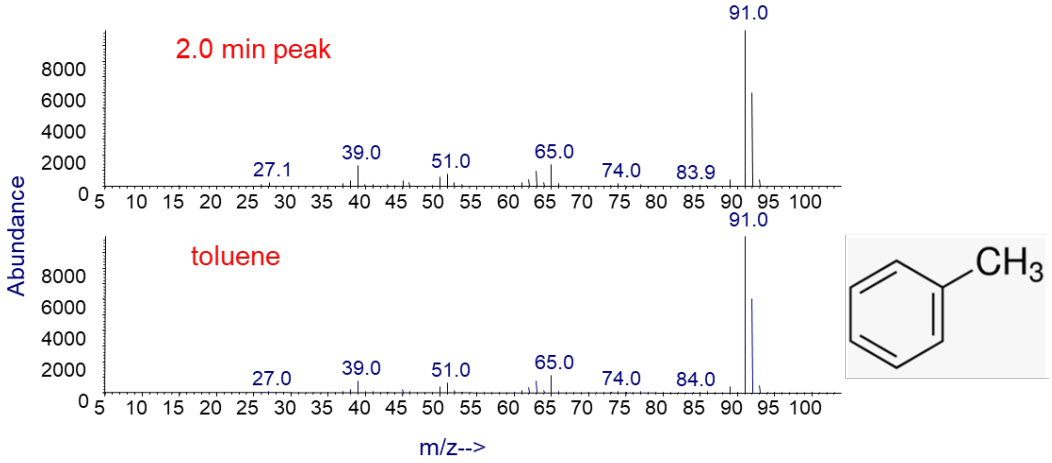


Fig. C-3 Mass spectrum and library search match (with structure) of 2.0-min peak from 650 °C pyrolysis of phenolic resin

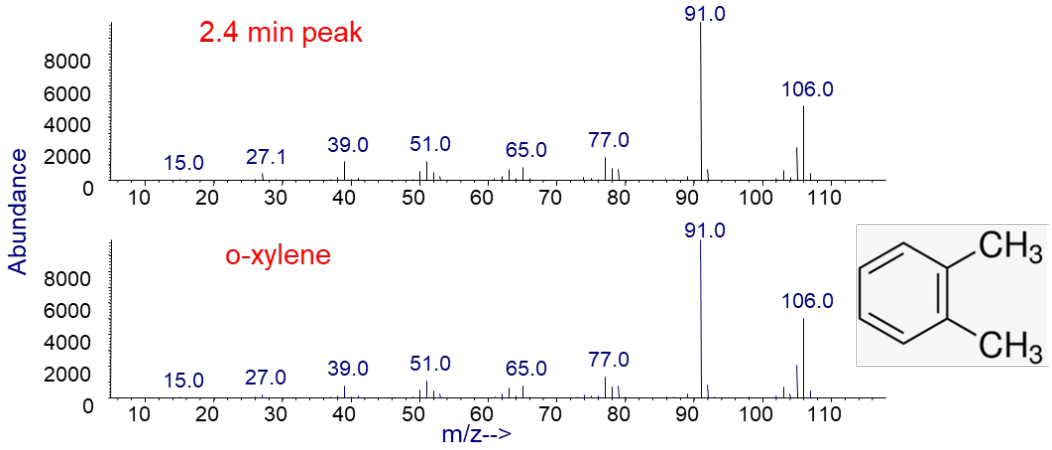


Fig. C-4 Mass spectrum and library search match (with structure) of 2.4-min peak from 650 °C pyrolysis of phenolic resin

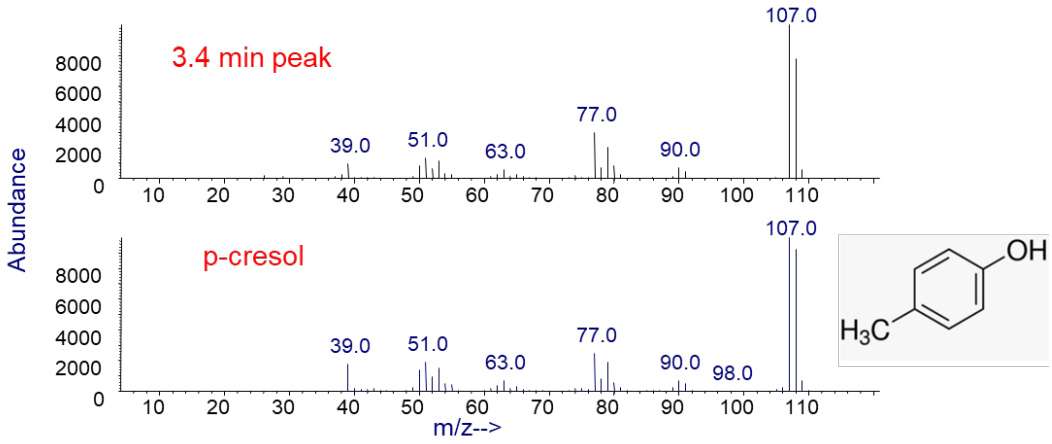


Fig. C-5 Mass spectrum and library search match (with structure) of 3.4-min peak from 650 °C pyrolysis of phenolic resin

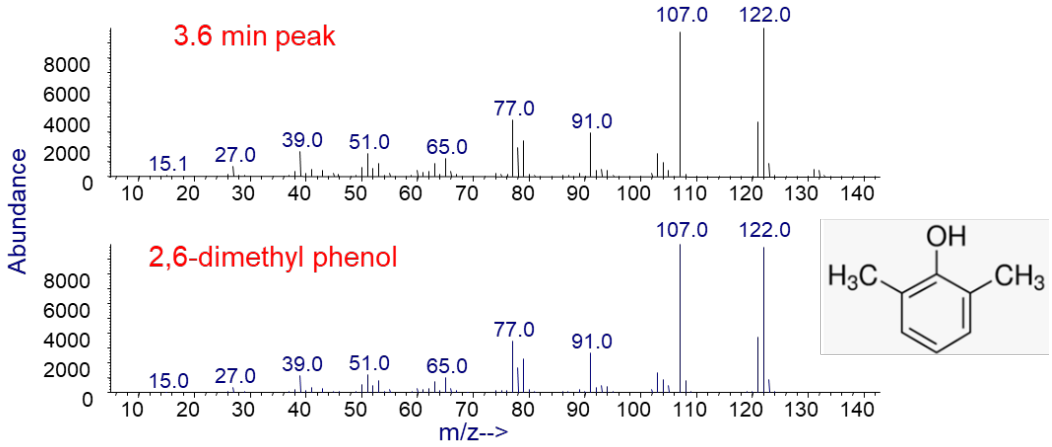


Fig. C-6 Mass spectrum and library search match (with structure) of 3.6-min peak from 650 °C pyrolysis of phenolic resin

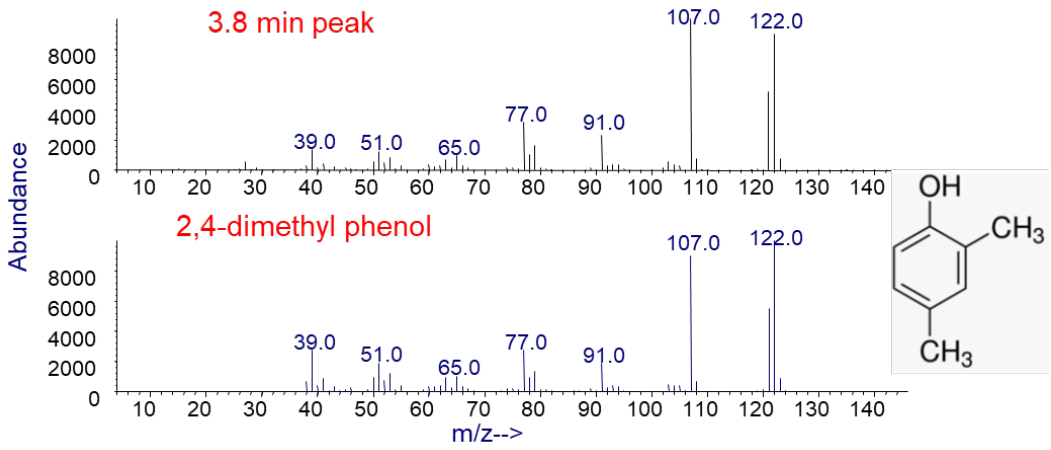


Fig. C-7 Mass spectrum and library search match (with structure) of 3.8-min peak from 650 °C pyrolysis of phenolic resin

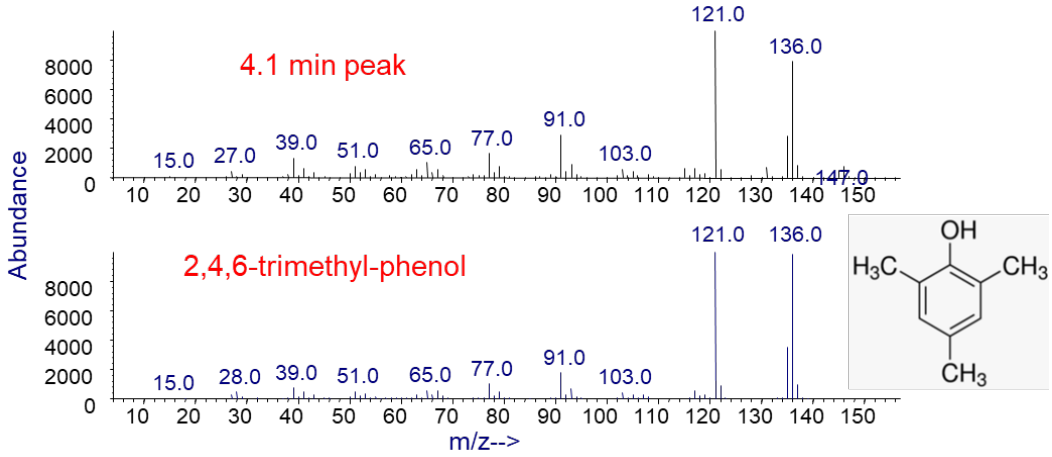


Fig. C-8 Mass spectrum and library search match (with structure) of 4.1-min peak from 650 °C pyrolysis of phenolic resin

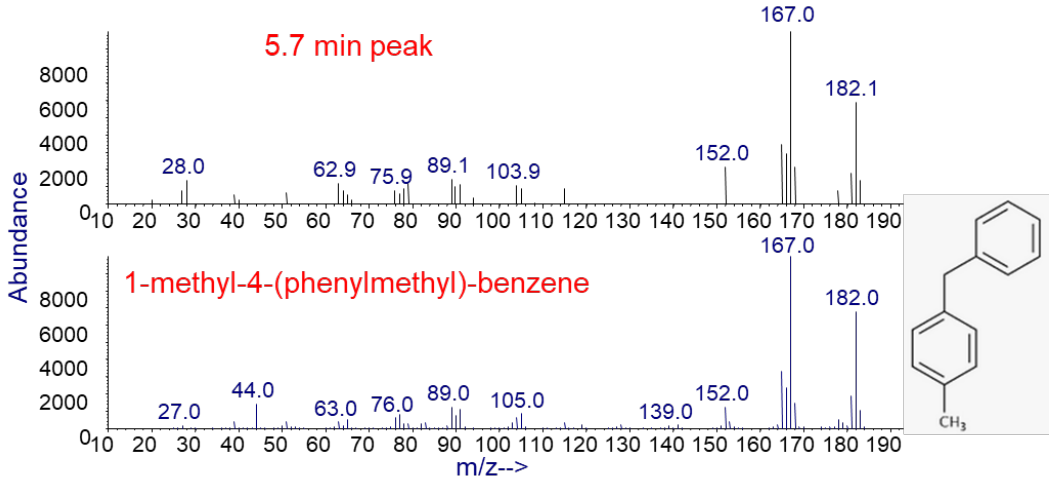


Fig. C-9 Mass spectrum and library search match (with structure) of 5.7-min peak from 650 °C pyrolysis of phenolic resin

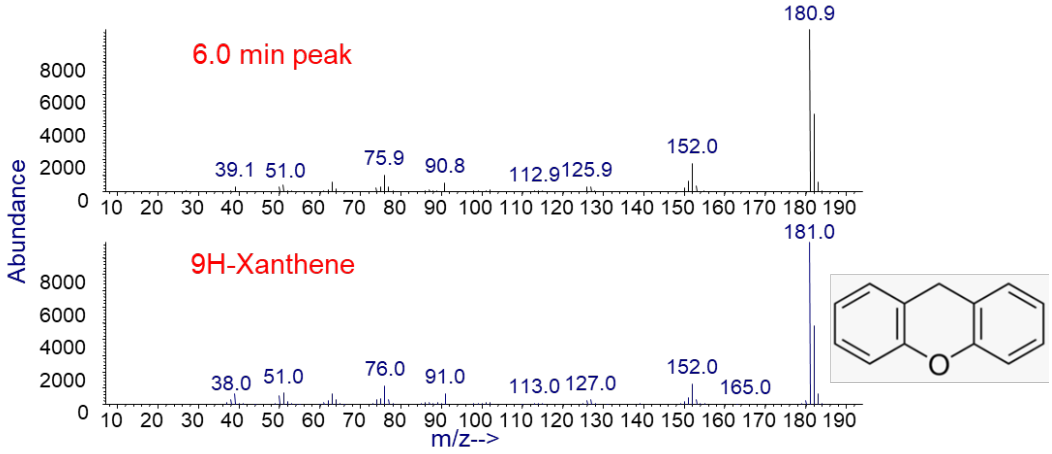


Fig. C-10 Mass spectrum and library search match (with structure) of 6.0-min peak from 650 °C pyrolysis of phenolic resin.

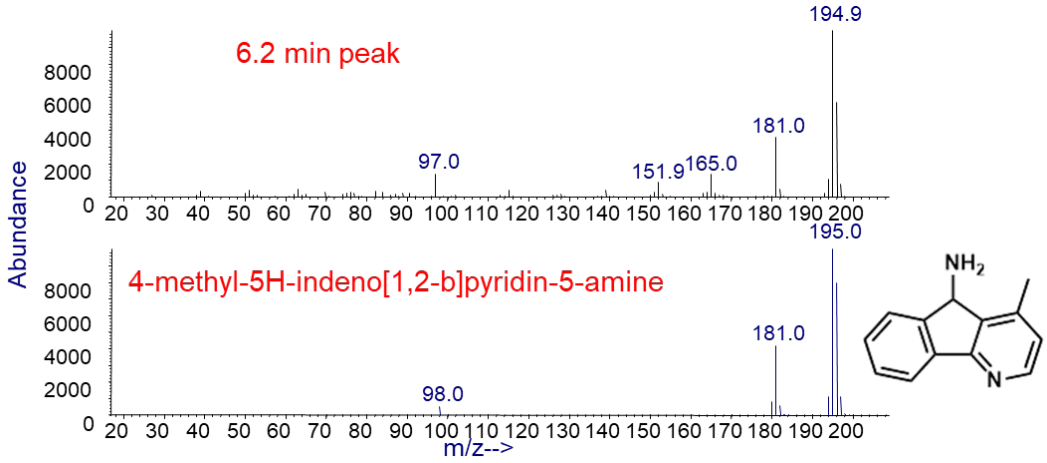


Fig. C-11 Mass spectrum and library search match (with structure) of 6.2-min peak from 650 °C pyrolysis of phenolic resin

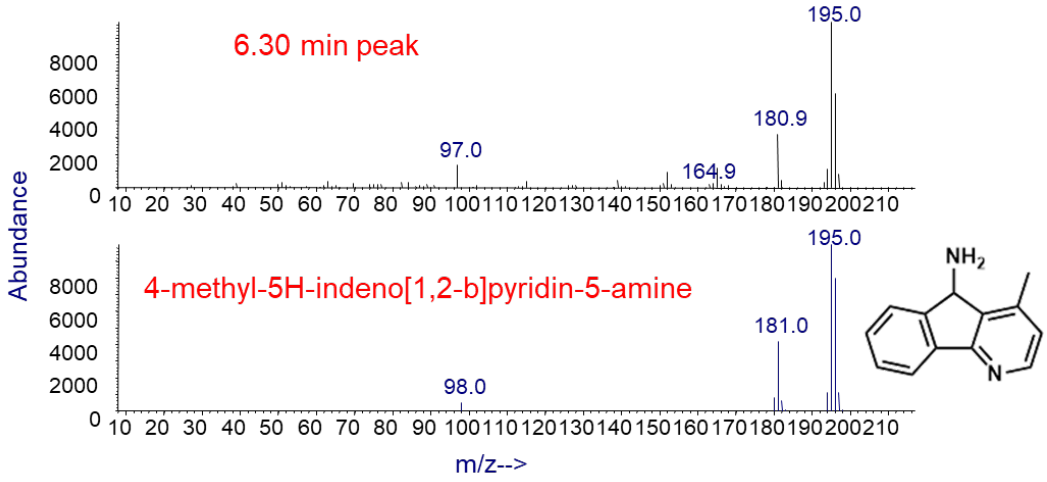


Fig. C-12 Mass spectrum and library search match (with structure) of 6.3-min peak from 650 °C pyrolysis of phenolic resin

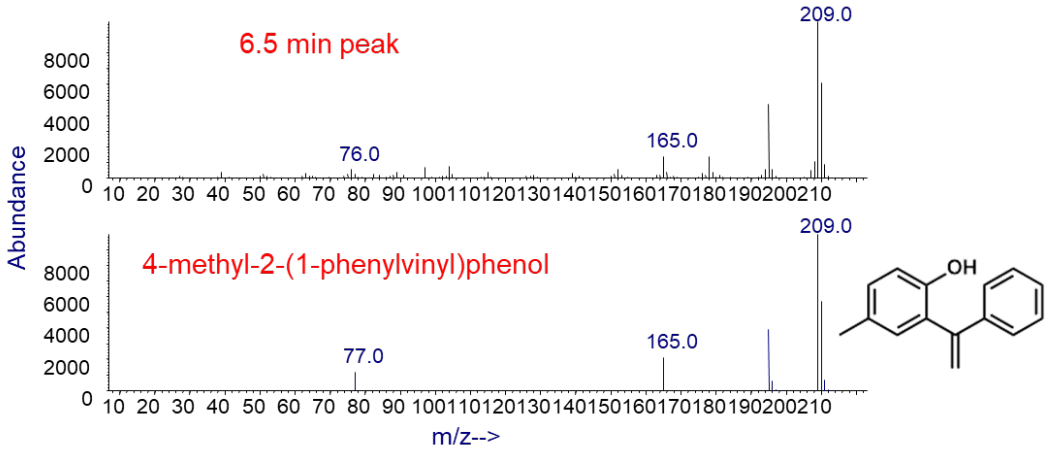


Fig. C-13 Mass spectrum and library search match (with structure) of 6.5-min peak from 650 °C pyrolysis of phenolic resin

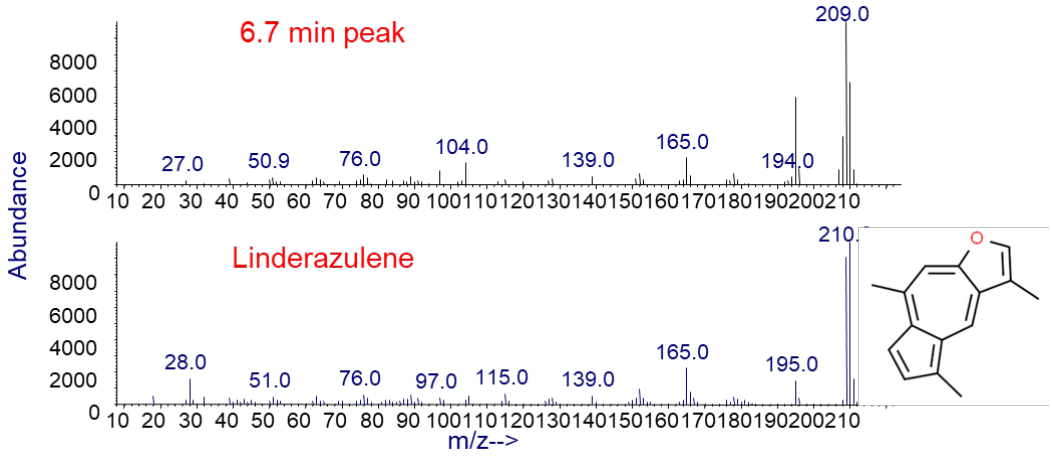


Fig. C-14 Mass spectrum and library search match (with structure) of 6.7-min peak from 650°C pyrolysis of phenolic resin

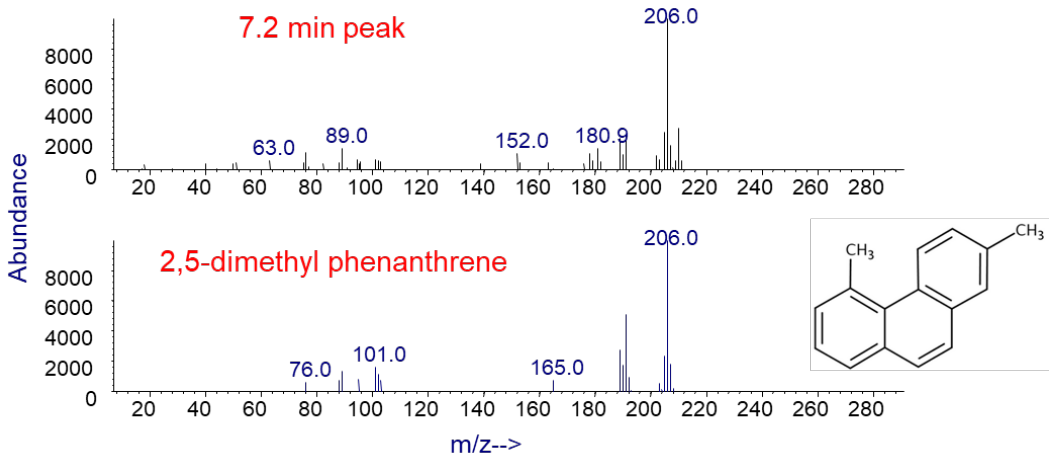


Fig. C-15 Mass spectrum and library search match (with structure) of 7.2-min peak from 650 °C pyrolysis of phenolic resin

Appendix D. Mass Spectra for 750 °C Pyrolysis

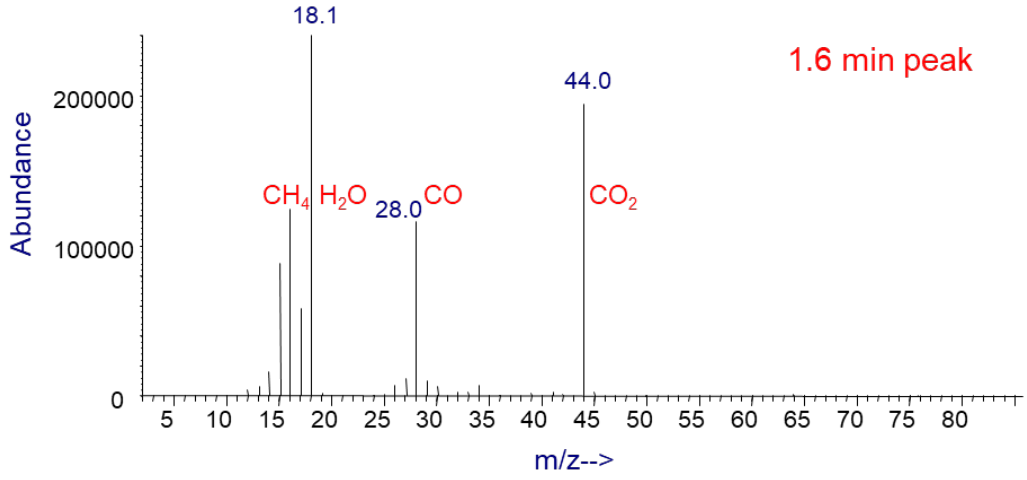


Fig. D-1 Mass spectrum of permanent gas peak from 750 °C pyrolysis of phenolic resin

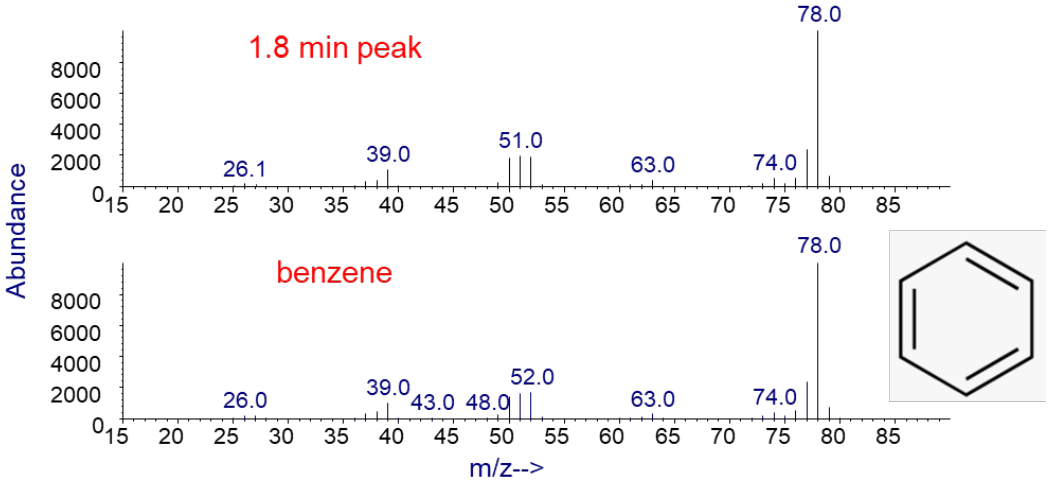


Fig. D-2 Mass spectrum and library search match (with structure) of 1.8-min peak from 750 °C pyrolysis of phenolic resin

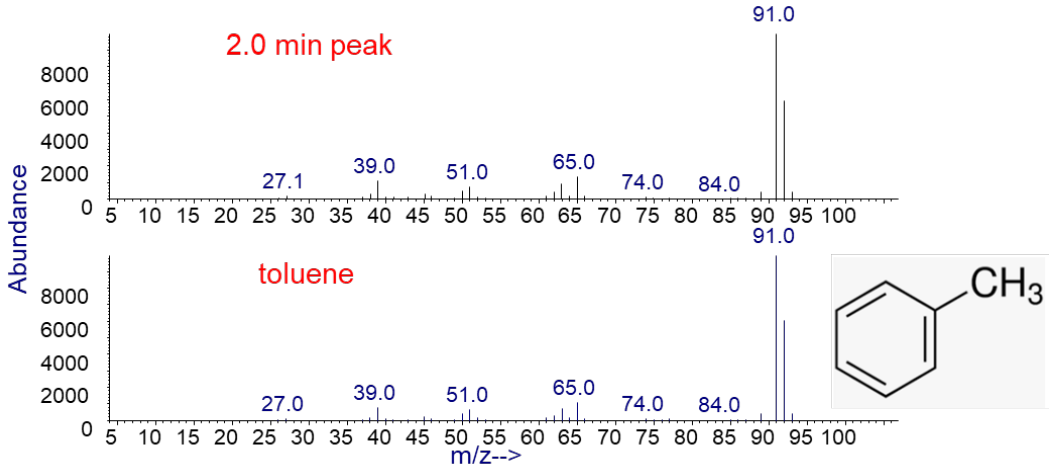
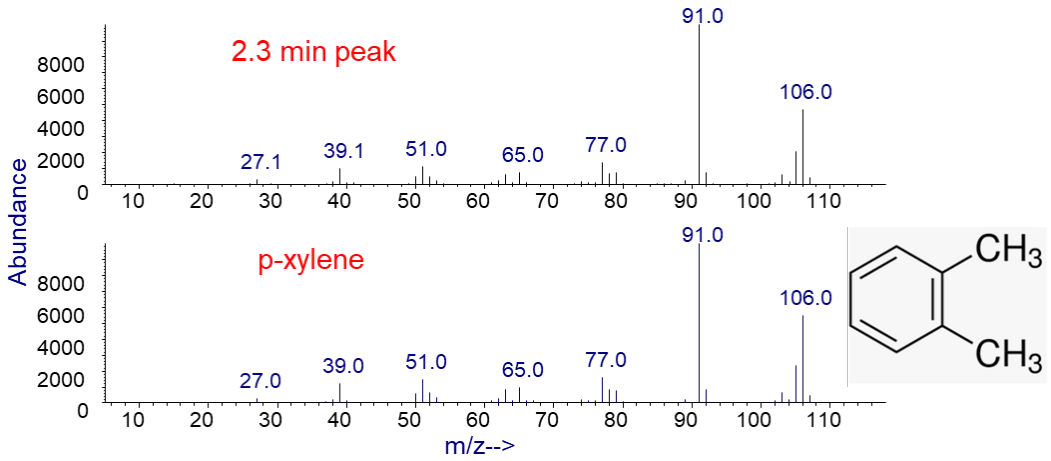


Fig. D-3 Mass spectrum and library search match (with structure) of 2.0-min peak from 750 °C pyrolysis of phenolic resin



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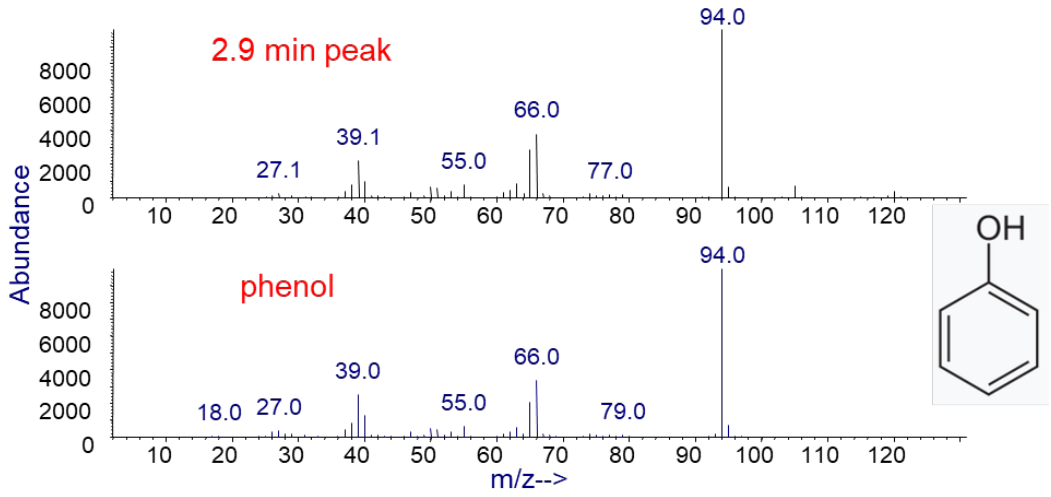

Fig. D-5 Mass spectrum and library search match (with structure) of 2.9-min peak from 750 °C pyrolysis of phenolic resin

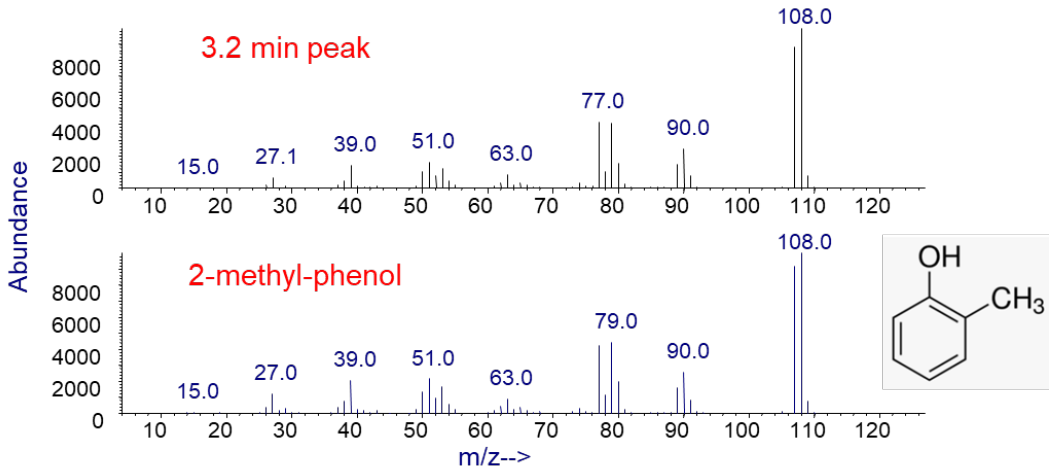

Fig. D-6 Mass spectrum and library search match (with structure) of 3.2-min peak from 750 °C pyrolysis of phenolic resin

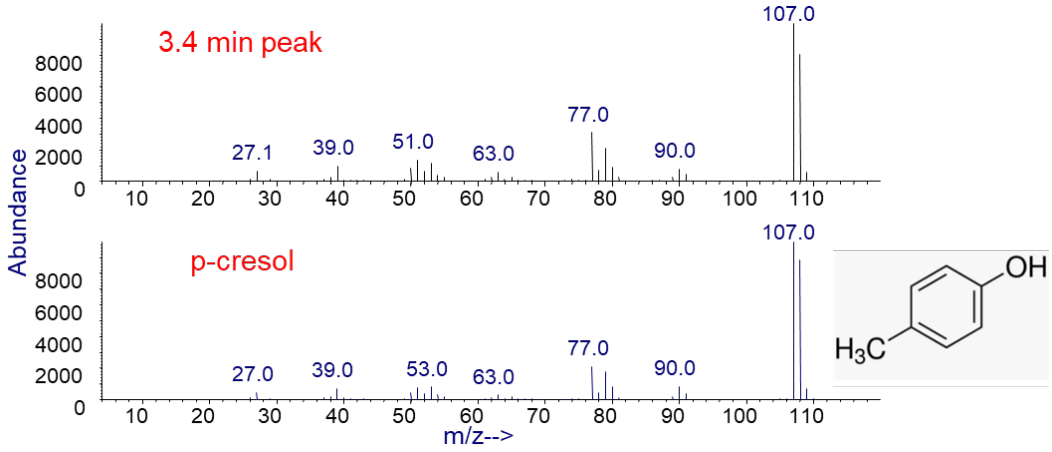

Fig. D-7 Mass spectrum and library search match (with structure) of 3.4-min peak from 750 °C pyrolysis of phenolic resin

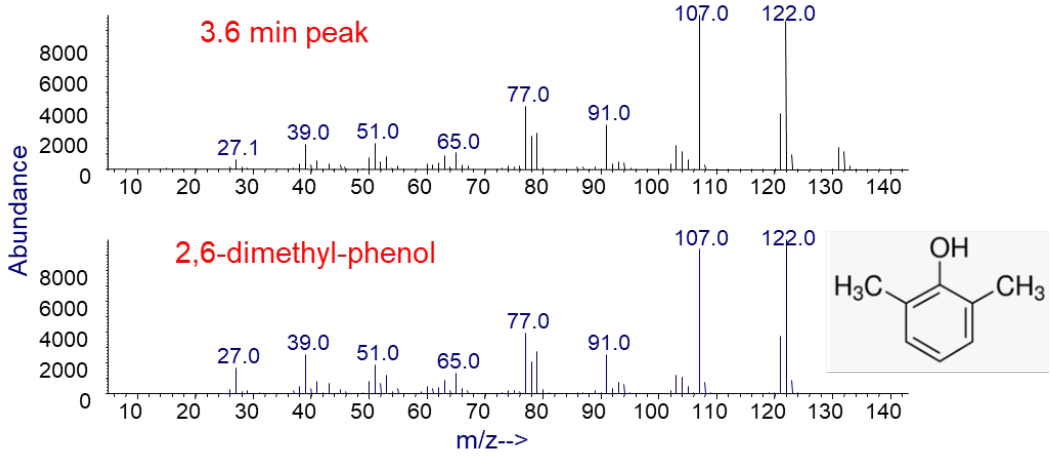

Fig. D-8 Mass spectrum and library search match (with structure) of 3.6-min peak from 750 °C pyrolysis of phenolic resin

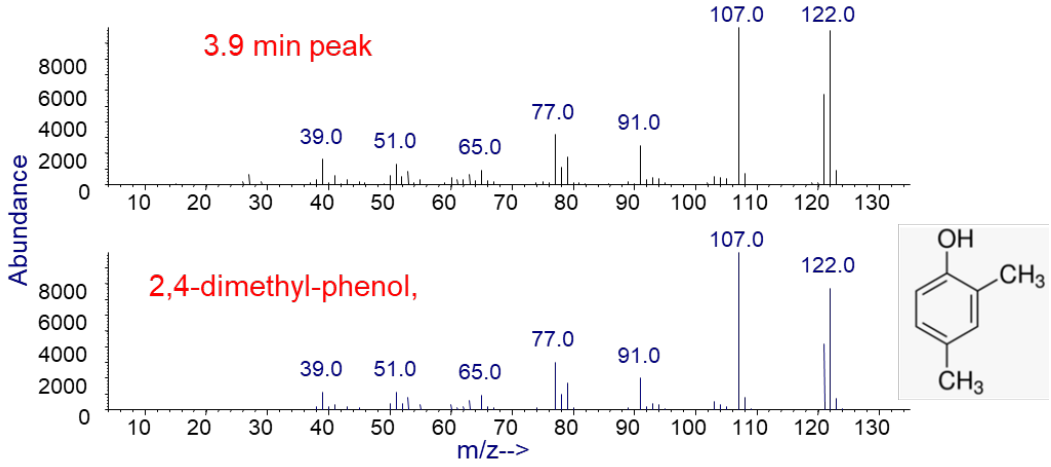

Fig. D-9 Mass spectrum and library search match (with structure) of 3.9-min peak from 750 °C pyrolysis of phenolic resin

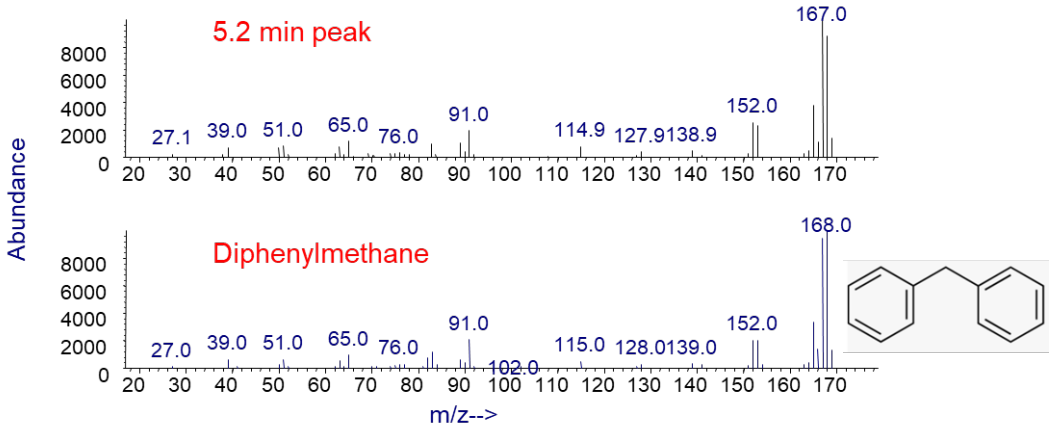

Fig. D-10 Mass spectrum and library search match (with structure) of 5.2-min peak from 750 °C pyrolysis of phenolic resin

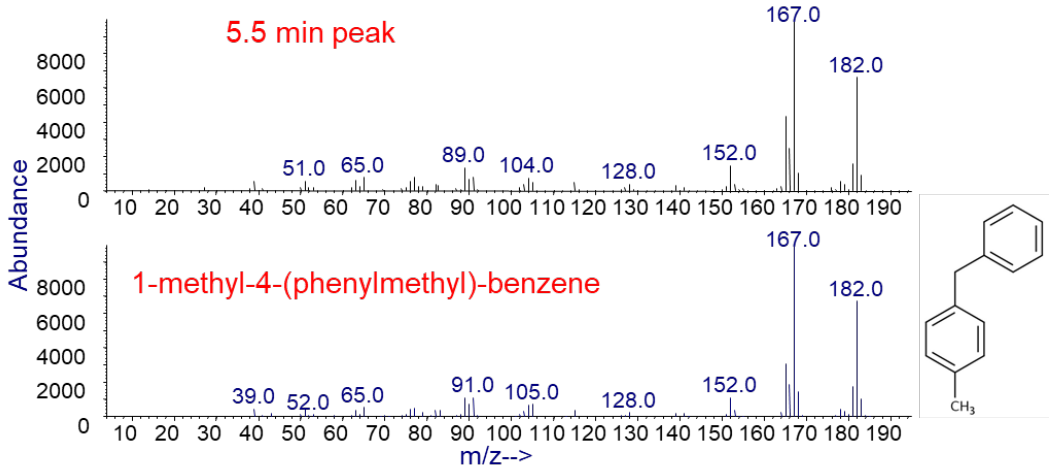

Fig. D-11 Mass spectrum and library search match (with structure) of 5.5-min peak from 750 °C pyrolysis of phenolic resin

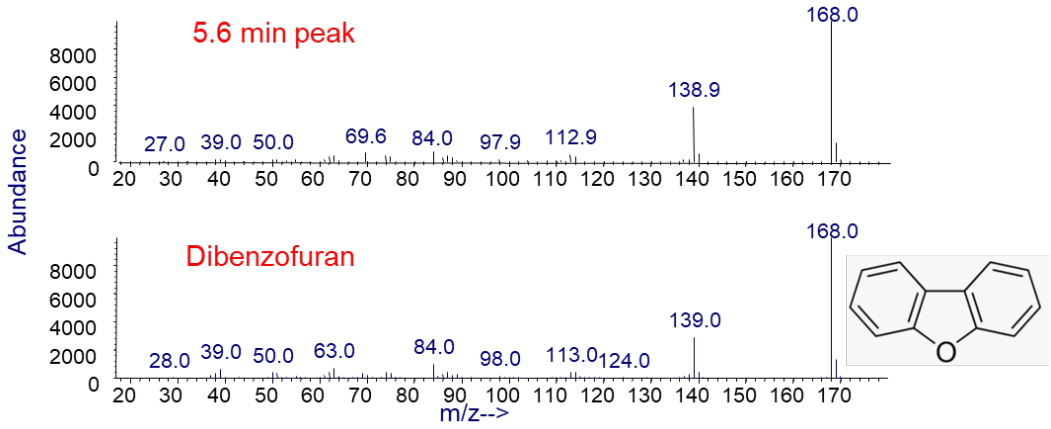

Fig. D-12 Mass spectrum and library search match (with structure) of 5.6-min peak from 750 °C pyrolysis of phenolic resin

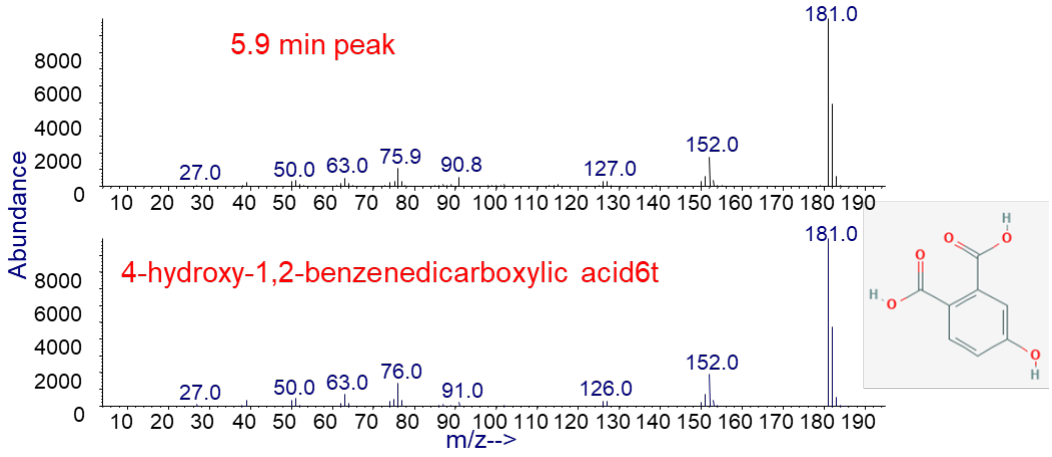

Fig. D-13 Mass spectrum and library search match (with structure) of 5.9-min peak from 750 °C pyrolysis of phenolic resin.

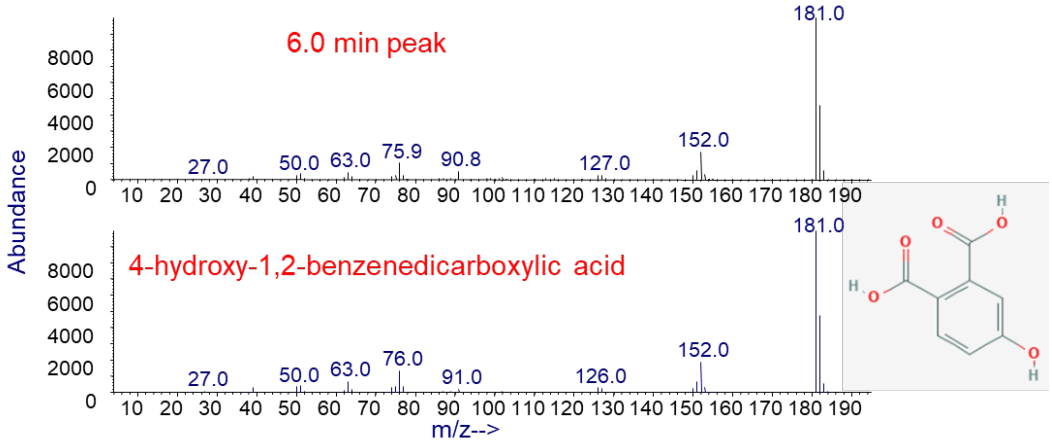

Fig. D-14 Mass spectrum and library search match (with structure) of 6.0-min peak from 750 °C pyrolysis of phenolic resin

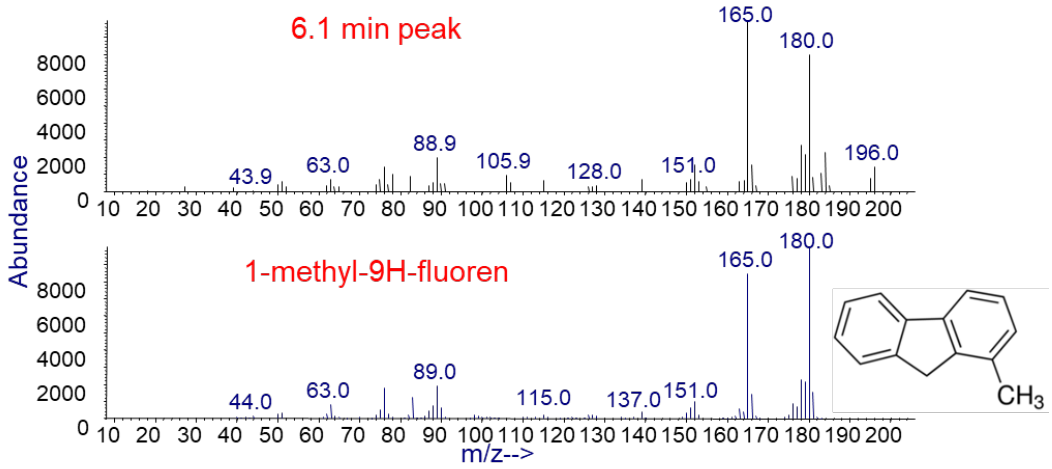

Fig. D-15 Mass spectrum and library search match (with structure) of 6.1-min peak from 750 °C pyrolysis of phenolic resin

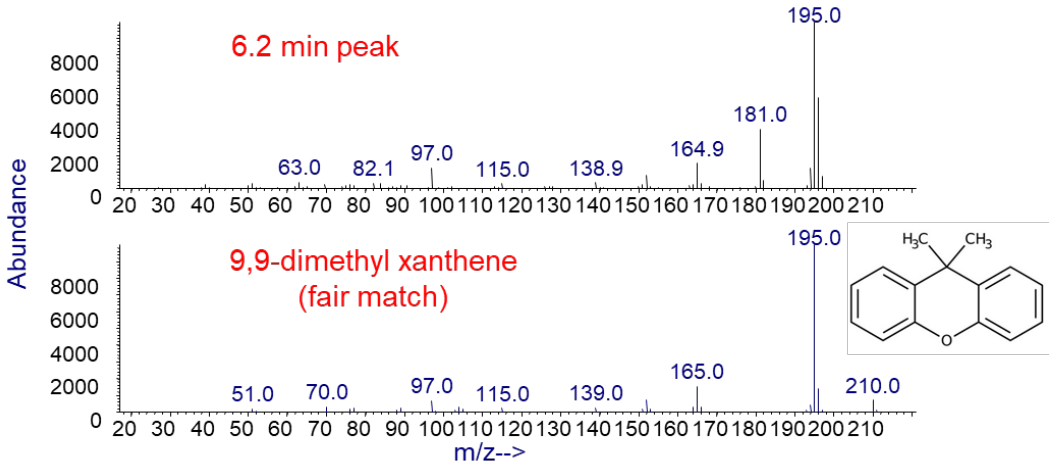

Fig. D-16 Mass spectrum and library search match (with structure) of 6.2-min peak from 750 °C pyrolysis of phenolic resin

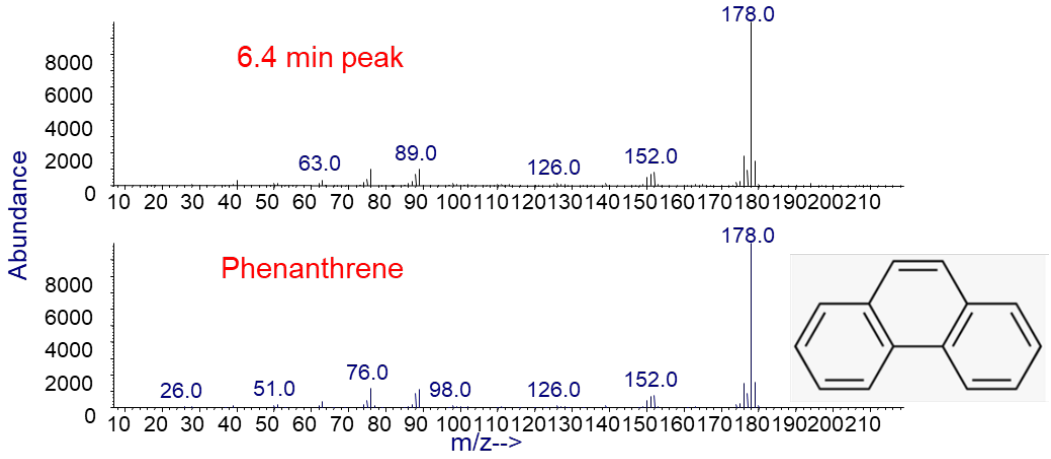

Fig. D-17 Mass spectrum and library search match (with structure) of 6.4-min peak from 750 °C pyrolysis of phenolic resin

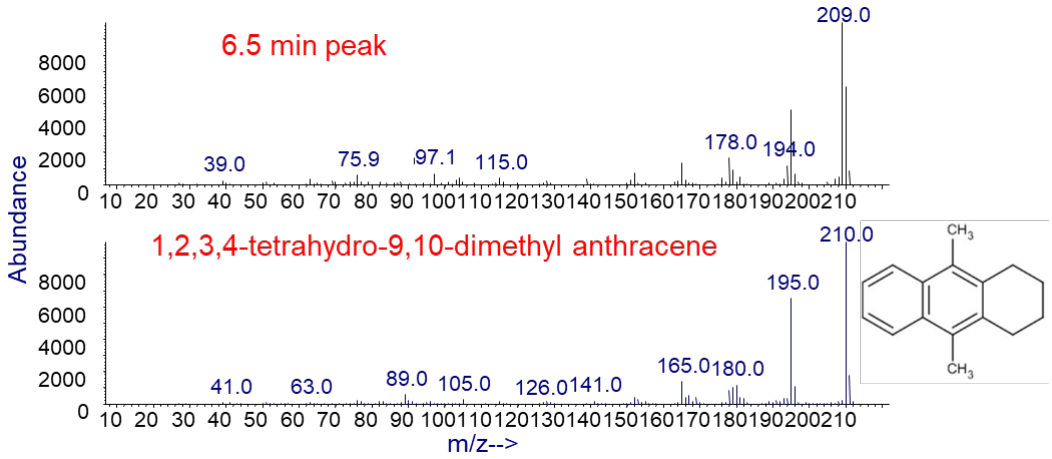

Fig. D-18 Mass spectrum and library search match (with structure) of 6.5-min peak from 750 °C pyrolysis of phenolic resin

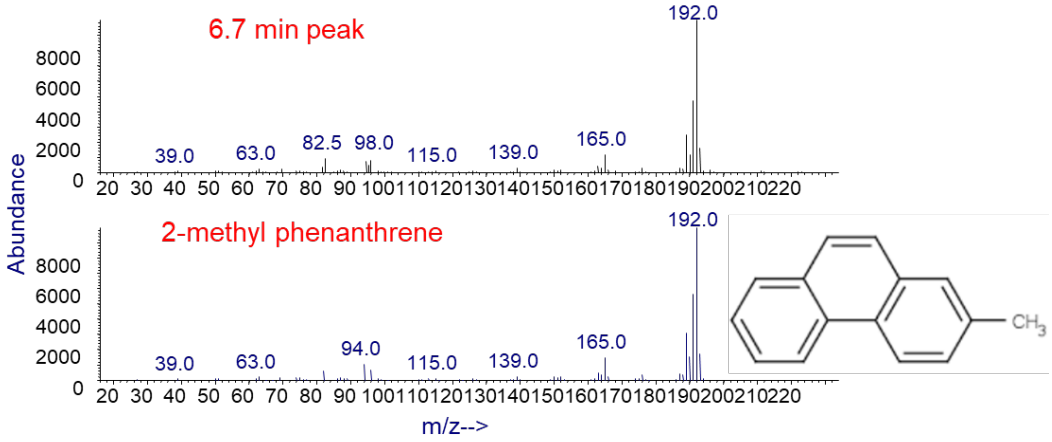

Fig. D-19 Mass spectrum and library search match (with structure) of 6.7-min peak from 750 °C pyrolysis of phenolic resin

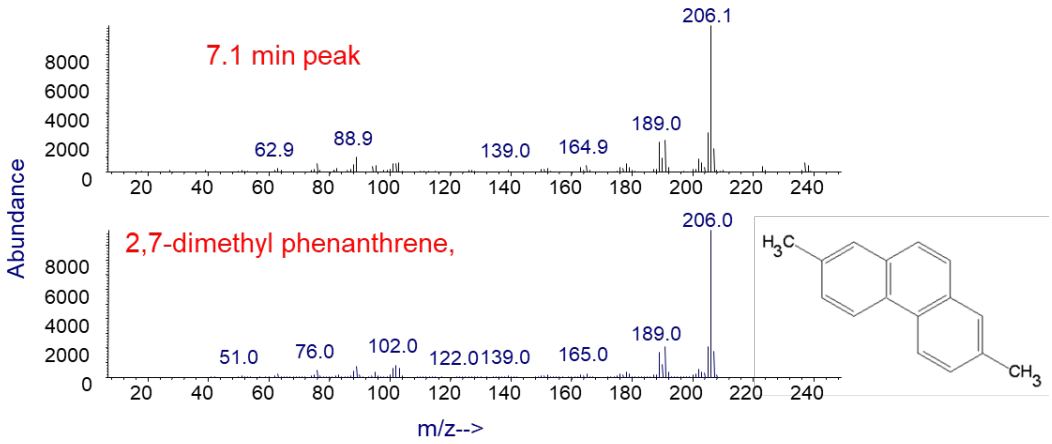

Fig. D-20 Mass spectrum and library search match (with structure) of 7.1-min peak from 750 °C pyrolysis of phenolic resin

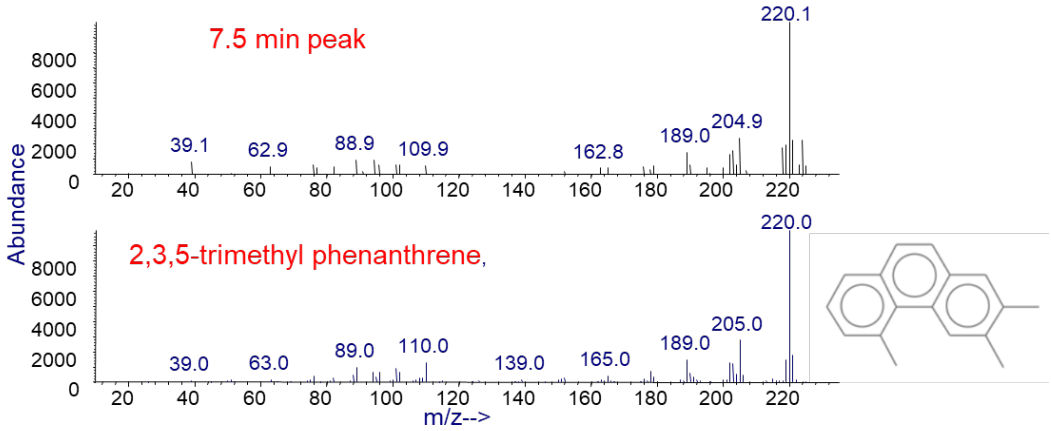

Fig. D-21 Mass spectrum and library search match (with structure) of 7.5-min peak from 750 °C pyrolysis of phenolic resin

Appendix E. Mass Spectra for 850 °C Pyrolysis

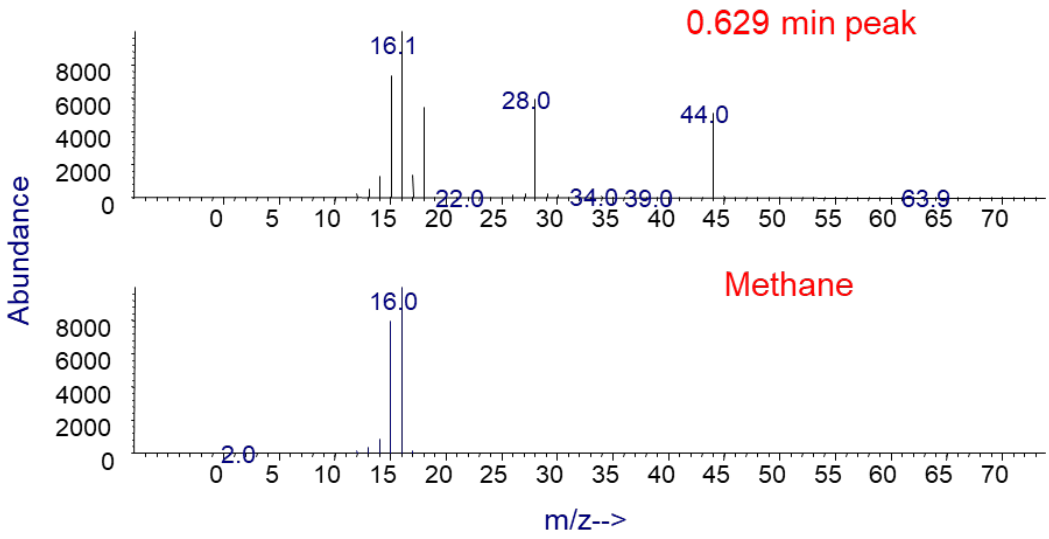

Fig. E-1 Mass spectrum of permanent gas peak from 850 °C pyrolysis of phenolic resin

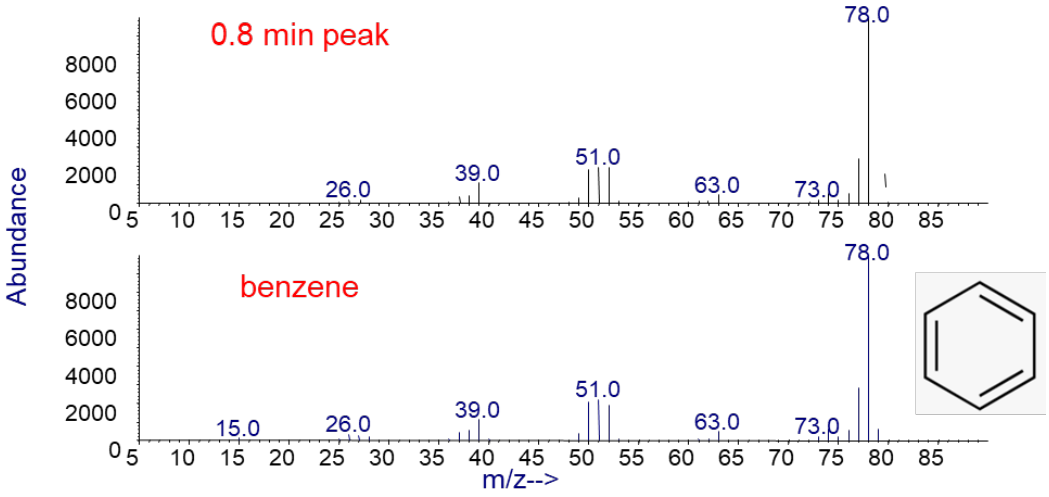

Fig. E-2 Mass spectrum and library search match (with structure) of 0.9-min peak from 850 °C pyrolysis of phenolic resin

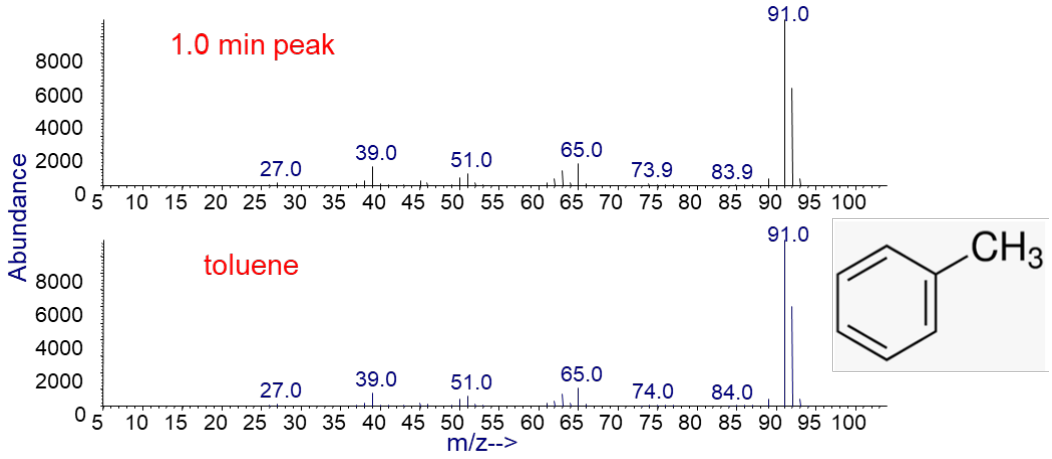

Fig. E-3 Mass spectrum and library search match (with structure) of 1.0-min peak from 850 °C pyrolysis of phenolic resin

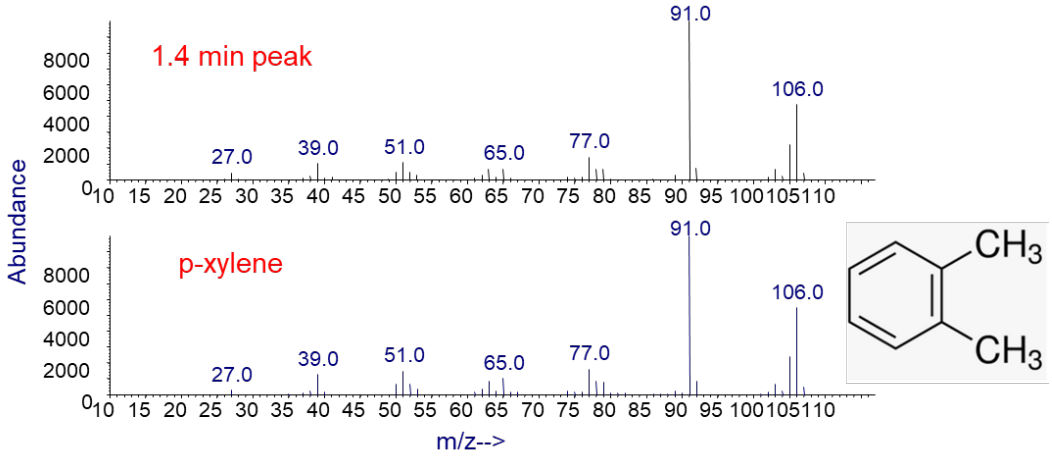

Fig. E-4 Mass spectrum and library search match (with structure) of 1.4-min peak from 850 °C pyrolysis of phenolic resin

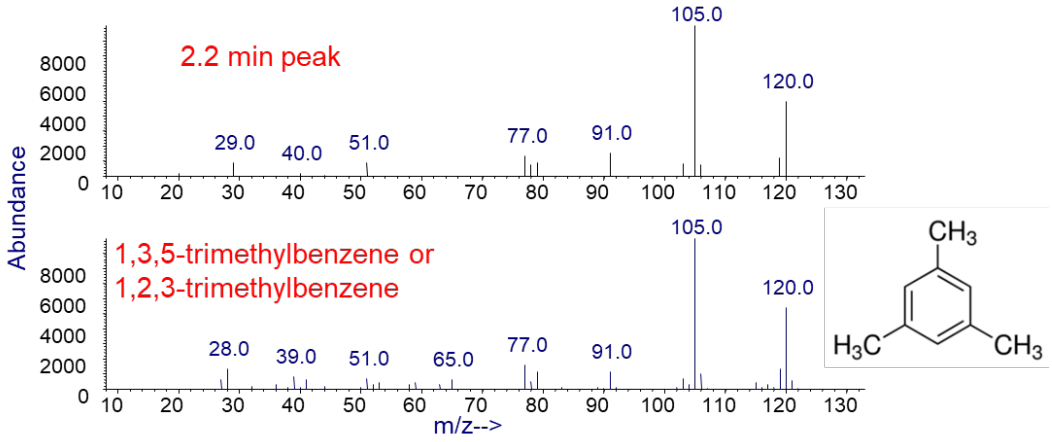

Fig. E-5 Mass spectrum and library search match (with structure) of 2.2-min peak from 850 °C pyrolysis of phenolic resin

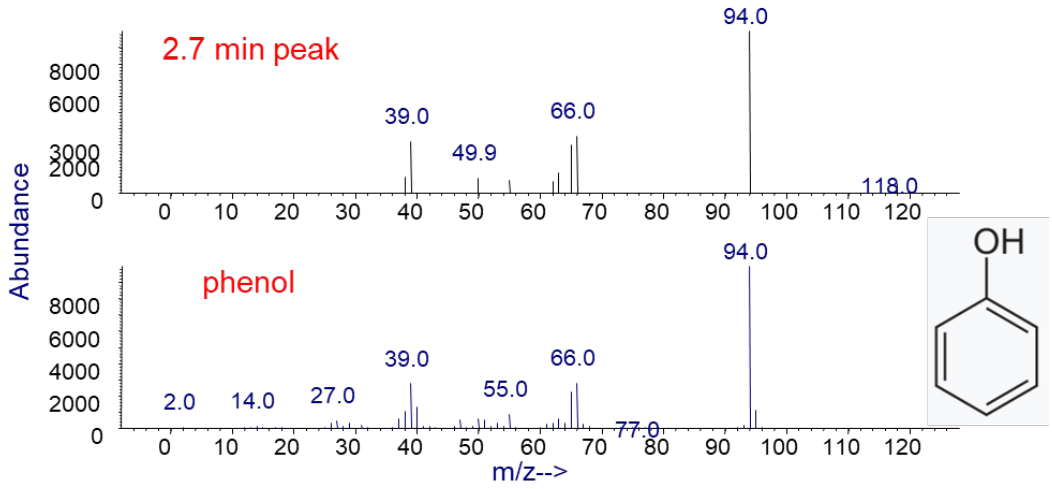

Fig. E-6 Mass spectrum and library search match (with structure) of 2.7-min peak from 850 °C pyrolysis of phenolic resin

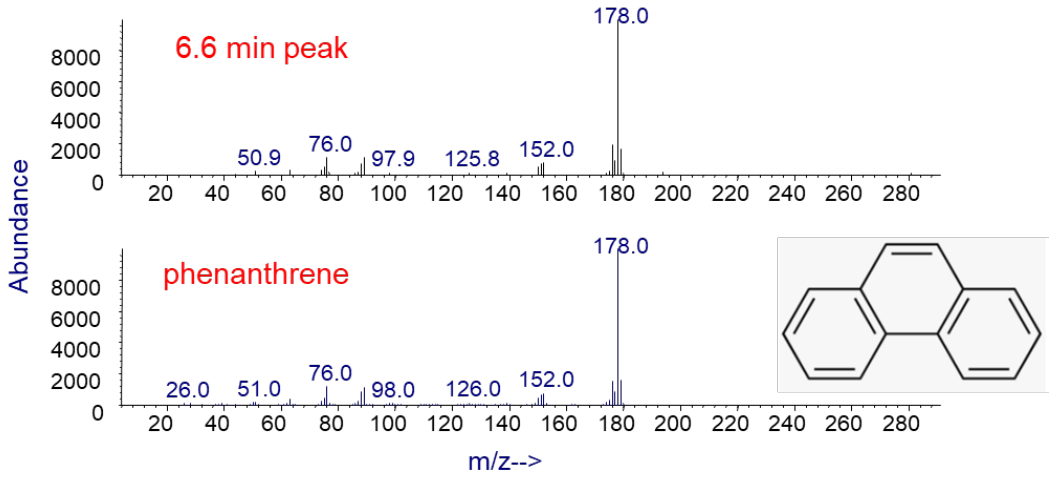

Fig. E-7 Mass spectrum and library search match (with structure) of 6.6-min peak from 850 °C pyrolysis of phenolic resin

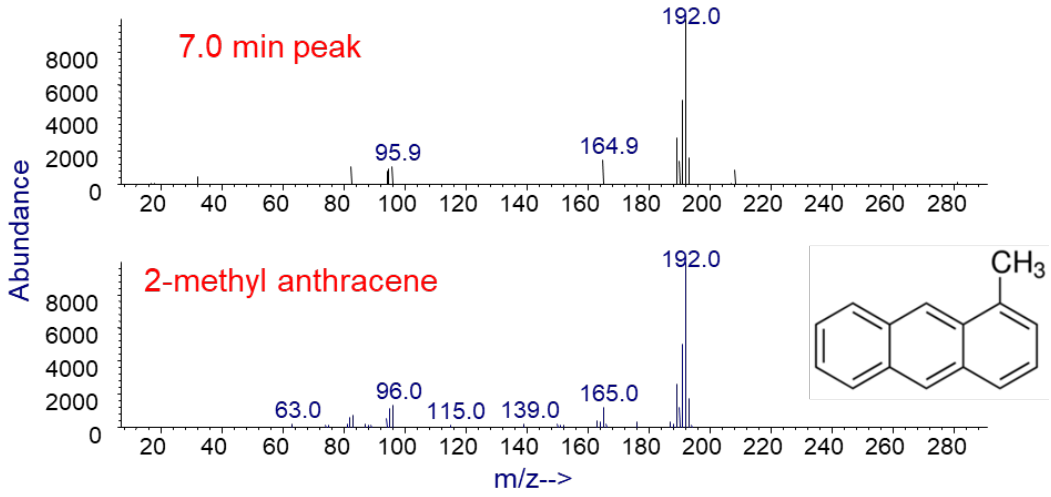

Fig. E-8 Mass spectrum and library search match (with structure) of 7.0-min peak from 850 °C pyrolysis of phenolic resin

Appendix F. Mass Spectra for 950 °C Pyrolysis

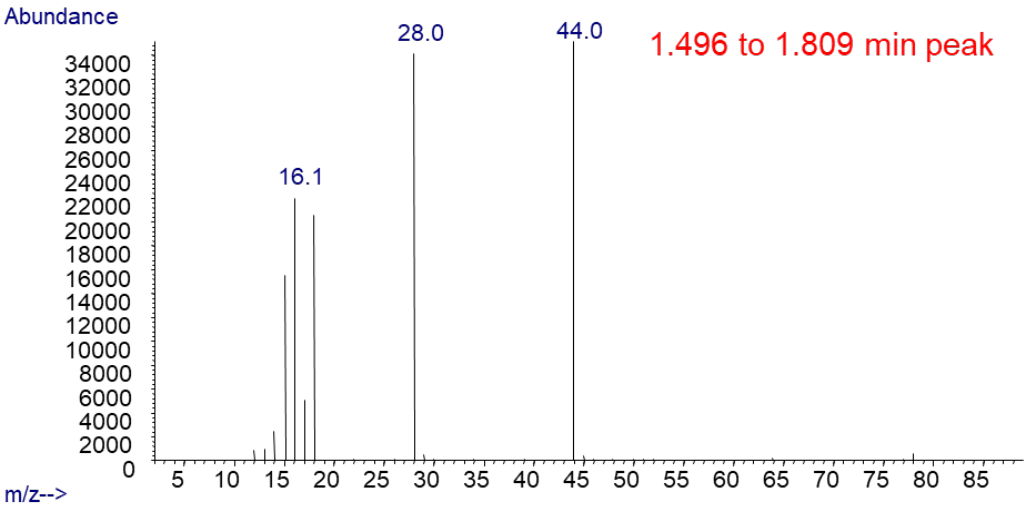

Fig. F-1 Mass spectrum of permanent gas peak from 950 °C pyrolysis of phenolic resin

Appendix G. Mass Spectra for 1050 °C Pyrolysis

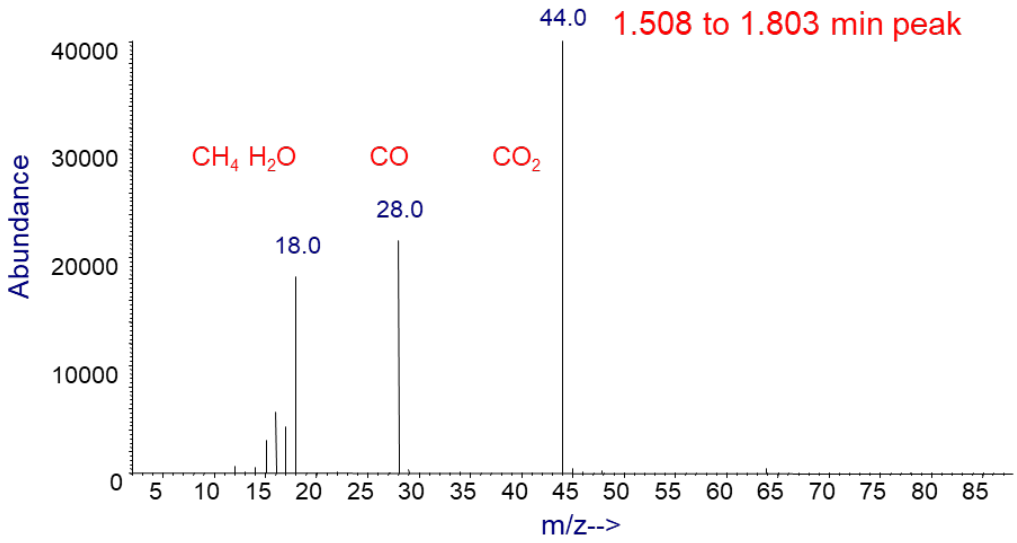

Fig. G-1 Mass spectrum of permanent gas peak from 1050 °C pyrolysis of phenolic resin

List of Symbols, Abbreviations, and Acronyms

CCDC ARL	US Army Combat Capabilities Development Command Army Research Laboratory
CO	carbon monoxide
CO_2	carbon dioxide
CH_4	methane
GC/MS	gas chromatography/mass spectrometry
H_2O	water

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